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A Market Basket Survey of Inorganic Arsenic in Food

R. A. SCHOOF¹*, L. J. YOST², J. EICKHOFF³, E. A. CRECELIUS,
D. W. CRAGIN⁴, D. M. MEACHER⁵ and D. B. MENZEL⁶

¹Exponent, Bellevue, WA, ²ENVIRON, Arlington, VA, ³Battelle Marine Sciences, Sequim, WA, ⁴Elf Atochem North America, Inc., Philadelphia, PA and ⁵University of California, Irvine, CA, USA

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Abstract—Dietary arsenic intake estimates based on surveys of total arsenic concentrations appear to be dominated by intake of the relatively non-toxic, organic arsenic forms found in seafood. Concentrations of inorganic arsenic in food have not been well characterized. Accurate dietary intake estimates for inorganic arsenic are needed to support studies of arsenic's status as an essential nutrient, and to establish background levels of exposure to inorganic arsenic. In the market basket survey reported here, 40 commodities anticipated to provide at least 90% of dietary inorganic arsenic intake were identified. Four samples of each commodity were collected. Total arsenic was analysed using an NaOH digestion and inductively coupled plasma–mass spectrometry. Separate aliquots were analysed for arsenic species using an HCl digestion and hydride atomic absorption spectroscopy. Consistent with earlier studies, total arsenic concentrations (all concentrations reported as elemental arsenic per tissue wet weight) were highest in the seafoods sampled (ranging from 160 ng/g in freshwater fish to 2360 ng/g in saltwater fish). In contrast, average inorganic arsenic in seafood ranged from less than 1 ng/g to 2 ng/g. The highest inorganic arsenic values were found in raw rice (74 ng/g), followed by flour (11 ng/g), grape juice (9 ng/g) and cooked spinach (6 ng/g). Thus, grains and produce are expected to be significant contributors to dietary inorganic arsenic intake. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: inorganic arsenic; dietary exposures; arsenic in food.

Abbreviations: DMA = dimethylarsenic acid; MMA = monomethylarsonic acid

INTRODUCTION

Arsenic has been detected in most foods tested. Although arsenic may be present in foods in a variety of organic compounds as well as in inorganic forms, most studies have reported only total arsenic concentrations. Based on studies in laboratory animals, inorganic arsenic may be a required nutrient for humans; however, the required intakes and the intakes from typical diets are not well characterized (Uthus, 1994a,b; Uthus and Seaborn, 1996). During the last two decades, much progress has been made in understanding the forms and concentrations of arsenic in some foods. The primary focus of prior research has been on arsenic in aquatic organisms, many of which contain total arsenic concentrations two to three orders of magnitude greater than total arsenic concentrations in foods of terrestrial origin

(Jelinek and Corneliusen, 1977; Schroeder and Balassa, 1966).

Studies of the arsenic forms found in finfish and shellfish have demonstrated that most arsenic in these foods occurs as methylated arsenic compounds, with only small amounts of inorganic arsenic present (Buchet *et al.*, 1994; Francesconi and Edmonds, 1994; Phillips, 1994; Yost *et al.*, 1998). Inorganic arsenic is not formed after ingestion of these compounds (Buchet *et al.*, 1994, 1996), indicating little or no metabolism in humans to the most toxic forms of arsenic. The complex arsenic compounds that predominate in marine organisms are much less acutely toxic than soluble inorganic arsenic compounds, with arsenobetaine (the predominant compound in finfish) being virtually non-toxic (Shiomi, 1994; Yamauchi and Fowler, 1994). Monomethylarsonic (MMA) and dimethylarsenic (DMA) acids are also less acutely toxic than the

*Corresponding author.

microwave oven, instead of being boiled in water. Commodities collected, a description of the samples, the state or country of origin of the raw commodity (if known), and a brief description of the preparation/cooking methods are presented in Table 1. Each sample was then analysed separately (i.e. no composites were prepared).

Sample analysis

All samples were analysed at Battelle Marine Sciences in Sequim, Washington. Total arsenic was analysed in food commodities after NaOH digestion by inductively coupled plasma-mass spectrometry (ICP-MS). Approximately one in every 10 samples was analysed in triplicate. For the digestion of liquids (milk, juices and water), NaOH was added to 8 g liquid to produce 2 N NaOH solution. This solution was heated for 16 hr at 80°C. For the digestion of solid food, either 1 or 2 g food was digested in 13 ml 2 N NaOH for 16 hr at 80°C. In preparation for ICP-MS analysis, 1 ml digestate was diluted with 9 ml 2% concentrated HNO₃. A model Elan 5000 Perkin-Elmer ICP-MS was operated using the stock cross-flow nebulizer. Several ions were monitored to evaluate polyatomic interference from Ar⁴⁰ Cl³⁵, which has the same mass as arsenic. When interference occurred, the manufacturer's correction factor was used to reduce the interference.

Food samples were digested for analysis of total arsenic using NaOH instead of HNO₃, which had been used in a previous study of arsenic in rice and yams (Schoof *et al.*, 1998). The NaOH digestion was expected to be more effective than HNO₃ in dissolving food with high fat content. A comparison between these two types of digestions on five different rice samples resulted in a relative percent difference of 10% between the mean concentrations. Total arsenic results for oyster tissue digested with NaOH or HNO₃ agreed within 5%. Analysis of standard reference bovine liver (certified 0.055 µg/g As) digested with NaOH resulted in 0.071 µg/g and digested with HNO₃ resulted in 0.062 µg/g. These results indicate that both digestion methods are comparable and accurate.

Arsenic speciation was determined in food samples digested with HCl. Between 0.5 and 2 g of food was digested with 13 ml 2 N HCl at 80°C for 16 hr. The digestates were stored at 4°C before analysis by EPA Method 1632, (US EPA, 1996). A 2-ml aliquot of the digestate was analysed for As³⁺ by arsine generation at pH 6 with the reducing agent sodium borohydride. The hydride was collected on a cryogenic column before quantification by atomic absorption (AA) using a quartz tube with an air-hydrogen flame positioned in the light path.

The HCl digestion is effective in dissolving the arsenic compounds in food without changing the oxidative states of As³⁺ and As⁵⁺ (Beauchemin

et al., 1988; Schoof *et al.*, 1998). Also, MMA and DMA are not decomposed during the digestion. Recovery of matrix spikes of As³⁺, As⁵⁺, MMA and DMA added to 21 different foods indicates that the digestion process does not alter the speciation of these four compounds. Mean spike recoveries for the four arsenic species were 92% for As³⁺, 86% for As⁵⁺, 89% for MMA and 98% for DMA. Because there are few published data on arsenic speciation in food, comparisons with other digestion methods are limited. The Canadian National Research Council reported the certified reference material DORM-1 (dogfish muscle) contained 0.47 ± 0.02 µg/g DMA (Beauchemin *et al.*, 1988). Our results for seven replicates of DORM-1, analysed with different batches of food, had a mean and standard deviation of 0.56 ± 0.07 µg/g. The concentrations of arsenic species were stable for over 1 month in the digestates of certified reference materials stored at 4°C.

The quantification of total inorganic arsenic, MMA and DMA was conducted similarly to that of As³⁺, except that arsines were generated at pH 1. The three arsines (arsine, methylarsine and dimethylarsine) were collected on the cold column, then quantified by AA when the column was heated. The different column retention times of the arsines allows quantification of inorganic arsenic, MMA and DMA. The concentration of As⁵⁺ is determined by the difference between inorganic arsenic and As³⁺. Every fourth sample was analysed in triplicate.

The data were blank-corrected by subtracting the mean of the procedural blanks. The mean blank concentrations are shown in Table 2. The method detection limits were determined from the variance in triplicate analyses of food samples containing low but detectable arsenic. The standard deviation was multiplied by the Student's *t*-value for 95% confidence level. The method detection limits are shown in Table 2.

If no arsenic was detected (after blank correcting), one-half the value of the method detection limit was given with a "U" flag. One-half the detection limit was used in subsequent calculations. Mean values have a "U" qualifier if all values used to calculate the mean were "U" qualified. When the concentration of arsenic in food (after blank correcting) was detected above the blank concentration but below the method detection limit, the value was "J" flagged. The same rule as was used for the "U" flagged values was also applied in assigning "J" qualifiers to mean values.

RESULTS

Table 3 shows mean concentrations of total and inorganic arsenic for 40 commodities and tap water. The data from the two towns from which food samples were collected did not differ significantly.

Table 2. Mean blank concentrations and method detection limits (ng/g wet weight)

	Mean blank concentrations	Method detection limits
As _{tot}	4.5*	3.6
As _i	1.9†	2
As ³⁺	< 1	1
As ⁵⁺	1.9†	2
MMA	< 1	1
DMA	< 2	2

Note: As_{tot}-total arsenicAs_i-inorganic arsenic

MMA-monomethylarsonic acid

DMA-dimethylarsinic acid.

Consequently, the data for all four samples of each commodity were averaged.

Total arsenic was detected in two or more samples of 35 of the 40 commodities, that is, all of the commodities except butter, soybean/vegetable oil, salt, whole milk and green beans. Inorganic arsenic was detected in two or more samples of 34 of the 40 commodities, that is, all commodities except soybean/vegetable oil, whole and skim milk, chicken, tuna and orange juice. Inorganic arsenic concentrations were either undetected or "J" qualified in approximately one-half of the samples, suggesting that the detection limits achieved in this study are just sufficient to characterize inorganic arsenic concentrations in a wide variety of foods.

Consistent with earlier studies, total arsenic concentrations (all concentrations reported as elemental arsenic per tissue wet weight) were highest in the four kinds of seafood sampled (means ranged from 160 ng/g in freshwater fish to 2360 ng/g in saltwater fish). In contrast, average inorganic arsenic mean concentrations in seafood ranged from less than 1 ng/g to 2 ng/g. Marked variation in total arsenic concentrations observed in finfish samples may reflect variations among species (Table 4). Concentrations were more consistent among canned tuna samples.

The next highest total arsenic concentrations occurred in rice (303 ng/g), which also had the highest concentrations of inorganic arsenic (Table 3). Other foods with relatively high (i.e. greater than 10 ng/g) total arsenic concentrations included foods high in protein (i.e. beef, chicken, pork, eggs and peanut butter) or sugar (i.e. beet sugar, cane sugar, grapes and grape juice), and grains (i.e. corn meal and flour).

The inorganic arsenic concentrations in raw rice (74 ng/g) were much higher than concentrations in other foods. The next highest concentrations of inorganic arsenic were in flour (11 ng/g), grape juice (9 ng/g), cooked spinach (6 ng/g), peanut butter (5 ng/g), peas (5 ng/g), as well as cane sugar, corn meal, cucumber and beet sugar (all 4 ng/g). Inorganic arsenic concentrations were low enough in most foods that it was not clear what arsenic forms predominated (i.e. As³⁺ or As⁵⁺); however,

in rice, flour, grape juice, spinach, peanut butter and cucumber, the concentrations of As³⁺ were generally more than twice the concentration of As⁵⁺. In contrast, cane sugar and beet sugar appeared to have more As⁵⁺ than As³⁺ (data not shown).

In fruits and vegetables, inorganic arsenic accounted for approximately one-half of the total arsenic (Table 3). In grains, sugars and oil, inorganic arsenic accounted for approximately one-quarter of the total arsenic, while only a small fraction of the total was inorganic in meat, poultry, fish and eggs. With a few exceptions, both MMA and DMA concentrations were undetected or very low. Rice and shellfish (shrimp) were the commodities with the highest DMA concentrations, with mean concentrations of 91 and 34 ng/g, respectively (Table 4). The next highest concentrations of DMA were in beet sugar and cane sugar, with concentrations of 7 and 8 ng/g, respectively (data not shown). DMA was also detected at low concentrations in seafood (Table 4), meat and fruits and fruit juices (data not shown). MMA was repeatedly detected only in samples of apple juice (data not shown) and rice (Table 4).

DISCUSSION

Inorganic arsenic was found at ng/g concentrations in most foods tested. Concentrations for inorganic arsenic reported in the present study were generally lower than those previously reported for seafood, meat and poultry, even though total arsenic concentrations were similar among studies. For example, while inorganic arsenic concentrations in saltwater finfish (cod, halibut, orange roughy, canned tuna) were less than 1 ng/g in the present study, three previous studies reported values from 5 to 28 ng/g for similar fish species (Buchet *et al.*, 1994; Mohri *et al.*, 1990; Yost *et al.*, 1998). Similarly, inorganic arsenic concentrations in shrimp ranged from 1 to 3 ng/g in the four samples tested in the present study, compared to values of 37 ng/g (Mohri *et al.*, 1990) and 100 ng/g (Yost *et al.*, 1998) in two samples tested previously. Meat and poultry products tested in the present study (N = 12) also contained 1 ng/g or less of inorganic arsenic, compared to 9 to 24 ng/g reported in a previous study (Yost *et al.*, 1998).

Inorganic arsenic concentrations in other foods were generally consistent with previously reported values. Inorganic arsenic concentrations have been notably consistent among rice samples tested by several methods, with average values ranging from 74 to 110 ng/g (Table 5). In particular, similar concentrations were reported for split samples analysed by hydride AA after HCl digestion or by ICP-MS after a water-based extraction (Table 5). Given these findings, it is unclear why lower inorganic arsenic concentrations were reported for seafood, meat and poultry in the present study compared to

Table 4. Arsenic concentrations in individual samples of selected foods (ng/g wet weight)

Sample	Total arsenic	Inorganic arsenic	MMA	DMA
Saltwater finfish				
Orange roughy	56E	1 U	0.5 U	1 J
Cod—sample 1	6080	0.3 J	0.5 U	5
Cod—sample 2	2320	0.1 J	0.5 U	4 J
Halibut	46E	0.7 J	0.5 U	0.7 J
Mean	2360	0.5 J	0.5 U	3
Canned tuna				
Sample 1	770	1 U	0.5 U	1 J
Sample 2	156	1 U	0.5 U	6
Sample 3	500	1 U	0.5 U	3
Sample 4	621	1 U	0.5 U	2 J
Mean	512	1 U	0.5 U	3
Shrimp				
Sample 1	1490	2 J	0.5 U	29
Sample 2	2790	2	0.5 U	57
Sample 3	475	1 J	0.5 U	21
Sample 4	2820	5	0.5 U	31
Mean	1890	1.9 J	0.5 U	34
Freshwater finfish				
Catfish—sample 1	25	2 J	0.5 U	1 U
Catfish—sample 2	31	1 U	0.5 U	1 U
Catfish—sample 3	29	0.2 J	0.5 U	1 U
Rainbow Trout	55E	1 U	0.5 U	4
Mean	160	1 J	0.5 U	2 J
Raw rice				
Sample 1	33E	5E	0.5 U	1 U
Sample 2	21E	6E	0.5 U	61
Sample 3	46E	81	3	202
Sample 4	19E	97	3	99
Mean	30E	73.7	2	91

Note: The fourth sample listed for all of the above foods is a mean of triplicate analyses for that sample.

J—estimates value observed above the blank concentration, but less than the method detection limit

U—not detected at method detection limit; one-half the detection limit shown.

in a subsequent article. However, typical inorganic arsenic intakes are not expected to exceed those reported previously (i.e. 8–14 µg/day for adults) (Yost *et al.*, 1998).

Although this study relies on one sampling event in one state, the commodities sampled originated from diverse geographic locations (Table 1). This diversity reflects the homogeneous nature of contemporary US food supplies. Most of the foods with the highest inorganic arsenic concentrations were processed foods that would not be expected to have a local origin (i.e. rice, grape juice, cooked spinach, peanut butter, peas, cane sugar, corn meal and beet sugar). Seasonal influences are also likely to be minimal in foods such as these that may be

stored for long periods without loss of quality. Consequently, the inorganic arsenic concentrations from this market basket survey are likely to be generally representative of typical concentrations in foods throughout the US.

Arsenic may serve an essential role in growth and nutrition (Uthus, 1994a,b; Uthus and Seaborn, 1996). Based on studies of arsenic deprivation in laboratory animals, an arsenic requirement for humans eating 2000 kcal/day has been estimated to be in the range of 12 to 25 µg/day (Uthus, 1994b). Deficiencies related to low arsenic intakes would be most likely to appear in individuals with altered arsenic homeostasis or metabolic stress (Uthus, 1994a). These doses should be compared to toxic

Table 5. Comparison of arsenic concentrations in rice (uncooked) (ng/g wet weight)

Source	Total arsenic	Inorganic arsenic	DMA	MMA
United States ^a (N = 4)	303	74	91	2
Taiwan ^b (N = 5)	120	83	21	21
Taiwan ^c (N = 5)	150	110	13	13
Canada ^d (N = 1)	240	100	—	—

^aPresent study (HCl digestion, hydride AA).

^bSchoof *et al.* (1998) (HCl digestion, hydride AA).

^cSchoof *et al.* (1998) (Split samples, ground, extracted with water and analysed by ICP-MS).

^dYost *et al.* (1998) (HCl/HBr digestion, hydride AA), "organic" arsenic reported to be 160 ng/g.